

PSRK Group Contribution Method for Predicting Phase Equilibria of Gas Hydrate

Ji-Ho Yoon,* Yoshitaka Yamamoto, Takeshi Komai and Taro Kawamura

*National Institute of Advanced Industrial Science and Technology (AIST)
Tsukuba, Ibaraki 305-8569, Japan*

Abstract

A thermodynamic model using the predictive Soave–Redlich–Kwong (PSRK) group contribution method to calculate the fugacities of all components in vapor and liquid phases coexisting hydrates is proposed. Since the PSRK method incorporated with the UNIFAC model takes into account the guest-guest interaction, the phase equilibria of mixed gas hydrates can be successfully reproduced. This approach greatly improves upon the accuracy of the modified Huron–Vidal second-order (MHV2) model, especially for three-guest hydrate systems. Based on experimentally determined X-ray data, an accurate representation for the molar volume of structure I (sI) hydrate is provided and used for predicting the equilibrium dissociation of methane hydrate at high pressures. Using this correlation, it is possible to reduce noticeable errors in dissociation predictions of high pressure hydrate-formers. Complete phase behavior including a new quadruple point, which is predicted to be 272.6 K and 7.55 MPa, for cyclopropane hydrate is presented by the proposed model calculation.

Introduction

The primary purpose of this article is to critically evaluate the predictive Soave–Redlich–Kwong (PSRK) group contribution method (Hollerbaum and Gmehling, 1991; Fisher and Gmehling, 1996; Gmehling et al., 1997; Horstmann et al., 2000) for predicting the phase equilibria of gas hydrate. In our previous work (Yoon et al., 2002), we developed a new model to predict the complicated phase behavior of simple and mixed gas hydrates. The Soave–Redlich–Kwong (SRK) equation of state (Soave, 1972) incorporated with the modified Huron–Vidal second-order (MHV2) mixing rule (Dahl and Michelsen, 1990) was used for calculating the fugacity of all components in the vapor and liquid phases. The modified UNIFAC group contribution model was also used as the excess Gibbs energy for the MHV2 model. Based on the van der Waals–Platteeuw theory with the Kihara spherical-core potential function (van der Waals and Platteeuw, 1959), this model could describe correctly some peculiar phase behaviors at lower and upper quadruple points and neighboring four three-phase curves around these quadruple points. However, the MHV2 model may have the disadvantage for describing the phase equilibria of multi-guest hydrate systems since it does not take into account the gas-gas (guest-guest) interaction, which is assumed to be zero. It should be also noted that the MHV2 model considers several light hydrocarbons such as ethane, propane, ethylene and propylene as new group components even though they can be treated without introducing new model parameters in the UNIFAC frame. Hollerbaum and Gmehling (1991) reported that these problems can be resolved clearly using the PSRK model by testing the vapor–liquid predictions for light hydrocarbon systems.

Recently, the classical thermodynamic approaches using fugacity equality between hydrate and water phases have been developed (Chen and Guo, 1998; Klada and

Sandler, 2000). These models removed the need for empirically fitting intermolecular parameters used in the van der Waals and Platteeuw model. Lee and Holder (2002) developed a method for gas hydrate equilibria using a variable reference chemical potential. They provided a correlation in terms of the molecular size of the guest component for estimating reference properties where experimental data are absent. However, for application of these methods to multicomponent systems, it still requires a lot of the guest-guest interaction parameters or Henry's law constants for describing the solubility behavior of guest molecules in water phase at high pressure. The use of the group contribution concept minimizes the parameter fitting or estimating efforts and has an advantage to accurately predict the phase behavior of macromolecular and multicomponent system without introducing new interaction parameters.

Thermodynamic Model for Phase Equilibria of Gas Hydrate

In previous work (Yoon et al., 2002), we presented a new expression for the fugacity of ice related to that of pure liquid water.

$$f_w^I = f_w^L \exp \left(- \int_{T_0}^T \frac{\Delta h_w^{fus}}{RT^2} dT + \int_0^P \frac{\Delta v_w^{fus}}{RT} dP \right) \quad (1)$$

This equation does not need the expression of the vapor pressure of ice and only uses the physical property difference between the ice and supercooled liquid water. Therefore, we can obtain a unique expression for the fugacity of water in the filled hydrate phase as follows

$$\hat{f}_w^H = f_w^L \exp \left[\frac{\Delta \mu_w^0}{RT} - \int_{T_0}^T \frac{\Delta h_w^{MT-I} + \Delta h_w^{fus}}{RT^2} dT + \int_0^P \frac{\Delta v_w^{MT-I} + \Delta v_w^{fus}}{RT} dP - \sum_m \nu_m \ln \left(1 + \sum_j C_{mj} \hat{f}_j^V \right) \right] \quad (2)$$

Here, the fugacities of supercooled water and all components in vapor phase, f_w^L and \hat{f}_j^V were calculated using the PSRK group contribution method combined with the UNIFAC model (Hansen et al., 1991).

The molar enthalpy difference between the ice and liquid water is given by

$$\Delta h_w^{fus} = \Delta h_w^{fus}(T_0) + \int_{T_0}^T \Delta C_p dT \quad (3)$$

Depending on the temperature range considered, the heat capacity difference between ice and liquid water ΔC_p is given by

$$\Delta C_p = \begin{cases} \Delta C_p^0 + \beta(T - T_0) & T \geq T_0 \\ C_1 + \frac{C_2}{T} + \frac{C_3}{T^2} + \frac{C_4}{T^3} & T_0 > T \geq T_H \\ D_1 + D_2 T + D_3 T^2 + D_4 T^3 - \frac{T - T_G}{T_H - T_G} \ln \frac{T - T_G}{T_H - T_G} & T_H > T > T_G \end{cases} \quad (4)$$

By the hyperquenching experiments, a new value for the glass transition temperature of supercooled water was found to be 165 K and recently reported in the literature (Velikov

et al., 2001). This temperature is about 30 K higher than the commonly accepted value over the past 50 years (Ghormley, 1957; McMillan and Los, 1965; Angell and Sare, 1970; Angell et al., 1973; Mishima and Stanley, 1998). On the basis of this revised value, we present here a new parameter set for the heat capacity difference between ice and liquid (or supercooled) water as follows; $\Delta C_p^0 = -38.13$, $\beta = 0.141$, $C_1 = -1.05253 \times 10^4$, $C_2 = 8.45606 \times 10^6$, $C_3 = -2.26357 \times 10^9$, $C_4 = 2.02637 \times 10^{11}$, $D_1 = -1.78631 \times 10^3$, $D_2 = 26.6606$, $D_3 = -1.35114 \times 10^{-1}$, $D_4 = 2.37259 \times 10^{-4}$, $T_H = 233$ K, and $T_G = 165$ K. For temperatures below T_G , the value of ΔC_p is assumed to be zero.

PSRK Group Contribution Method

The PSRK group contribution method is based on the SKR equation of state

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)} \quad (5)$$

where the mixture parameter b is derived from the conventional mixing rule

$$b = \sum_{i=1}^n x_i b_i \quad (6)$$

Huron and Vidal (1979) originally developed a new method for deriving a mixing rule in connection with the excess Gibbs energy, and thus they obtained an equation relating excess Gibbs energy at infinite pressure to the a/b parameter of the SRK equation of state using the following equation

$$g_\infty^E = RT \left[\ln \varphi - \sum_{i=1}^n x_i \ln \varphi_i \right] \quad (7)$$

where φ and φ_i are the fugacity coefficients of the solution mixture and pure component i , respectively. Michelsen (1990a,b) proposed a modified formulation of the Huron–Vidal mixing rule which uses the SRK equation of state and a reference pressure of zero. The resulting equation could be obtained in the following explicit form

$$q_1 \left(\alpha - \sum_{i=1}^n x_i \alpha_i \right) + q_2 \left(\alpha^2 - \sum_{i=1}^n x_i \alpha_i^2 \right) = \frac{g_0^E}{RT} + \sum_{i=1}^n x_i \ln \left(\frac{b}{b_i} \right) \quad (8)$$

where $\alpha = a/bRT$ and $\alpha_i = a_i/b_iRT$. The recommended values of q_1 and q_2 for the modified Huron–Vidal first-order (MHV1) mixing rule are -0.539 and 0 , respectively, and those for the MHV2 mixing rule are -0.478 and -0.0047 , respectively (Dahl and Michelsen, 1990). The simplest first-order approximation is used in the PSRK model

$$\alpha = \frac{1}{A_1} \left[\frac{g_0^E}{RT} + \sum_{i=1}^n x_i \ln \left(\frac{b}{b_i} \right) \right] + \sum_{i=1}^n x_i \alpha_i \quad (9)$$

The recommended value of $A_1 = q_1 = -0.539$ has been changed to $A_1 = -0.64663$ in the PSRK model, which yields better results at higher pressures (Holderbaum and Gmehling, 1991).

Results and Discussion

As shown in Table 1, the lattice and thermodynamic properties of empty hydrate lattice suggested by Parrish and Prausnitz (1972) are used in the model calculation because their values give a very good agreement between experimental and calculated

hydrate dissociation pressures.

Table 1. Lattice and Thermodynamic Properties of Gas Hydrates Used in This Study

	Structure I	Structure II
Ideal structure ^a	3M ₁ ·M ₂ ·23H ₂ O	M ₁ ·2M ₂ ·17H ₂ O
Number of water molecules / unit cell	46	136
Number of small cavities / unit cell	2	16
Number of large cavities / unit cell	6	8
Average radius of small cavities, Å	3.95	3.91
Average radius of large cavities, Å	4.3	4.73
Coordination number of small cavities	20	20
Coordination number of large cavities	24	28
$\Delta\mu_w^0$, J/mol	1264	883
Δh_w^{MT-I} , J/mol	1151	808
Δv_w^{MT-I} , cm ³ /mol	3.0	3.4
Δh_w^{fus} , J/mol		−6011
Δv_w^{fus} , cm ³ /mol		1.6

^a M₁ and M₂ are large and small cavities, respectively.

In our previous work (Yoon et al., 2002), we did not take into account the compressibility of gas hydrate and therefore the effect of pressure on the hydrate lattice was assumed to be negligible. It should be noted, however, that this simple approach may result in some large deviations between experimental and predicted dissociation pressures for methane hydrate, particularly at high pressure conditions over 100 MPa (Klauda and Sandler, 2000). Based on experimental X-ray diffraction data (Tse, 1987; Hirai et al., 2000), the molar volume of empty hydrate lattice for each structure has been expressed as a function of temperature and pressure (Klauda and Sandler, 2000).

$$v_{w,I}^{MT}(T, P) = (11.835 + 2.217 \times 10^{-5} T + 2.242 \times 10^{-6} T^2)^3 \frac{10^{-30} N_A}{46} - 8.006 \times 10^{-9} P + 5.448 \times 10^{-12} P^2 \quad (10)$$

$$v_{w,II}^{MT}(T, P) = (17.13 + 2.249 \times 10^{-4} T + 2.013 \times 10^{-6} T^2 + 1.009 \times 10^{-9} T^3)^3 \frac{10^{-30} N_A}{136} - 8.006 \times 10^{-9} P + 5.448 \times 10^{-12} P^2 \quad (11)$$

where N_A is the Avogadro's number and T and P are the equilibrium temperature and pressure given in K and MPa units, respectively. When comparing with the values calculated from X-ray diffraction data for methane hydrate at high pressure conditions (Hirai et al., 2000), the molar volume predicted using these equations is within an average percent absolute deviation (% AAD) of 2.5. In present study, the suggested approach is also used to resolve inaccuracies for methane hydrate and applied to all gas hydrate-formers. For more accurate prediction, we propose the revised parameters for the molar volume of sI hydrate as follows.

$$v_{w,I}^{MT}(T, P) = (11.835 + 2.217 \times 10^{-5} T + 2.242 \times 10^{-6} T^2)^3 \frac{10^{-30} N_A}{46} + 1.6155 \times 10^{-9} P - 2.5054 \times 10^{-12} P^2 + 2.2561 \times 10^{-14} P^3 \quad (12)$$

This equation is in an excellent agreement with the experimental values and therefore the % AAD is less than 0.1. For convenience, we call PSRK and MHV2 with the correlation depending on temperature and pressure, PSRK-VT and MHV2-VT, respectively.

Table 2. Average Absolute Deviations of Predicted Hydrate Dissociation Pressures of Simple Gas Hydrates

Guest	T , K	P , MPa	N_p	% AAD			
				MHV2	MHV2-VT	PSRK	PSRK-VT
CH ₄	148–320	0.005–400	92	9.3	4.7 (6.8) [†]	6.7	4.4 (5.7)
C ₂ H ₆	200–288	0.008–3.3	59	2.0	1.8 (1.8)	1.9	1.9 (1.9)
C ₂ H ₄	269–305	0.47–103	63	5.5	3.8 (4.7)	5.4	3.6 (5.1)
C ₃ H ₈	247–279	0.04–0.57	65	3.2	<i>n.a.</i> [‡]	3.3	<i>n.a.</i>
C ₃ H ₆	273–274	0.46–0.60	15	0.6	<i>n.a.</i>	0.8	<i>n.a.</i>
CO ₂	151–283	0.0005–4.4	92	3.1	3.0 (3.0)	2.9	2.8 (2.9)
O ₂	267–291	9.9–95	50	2.5	<i>n.a.</i>	2.3	<i>n.a.</i>
N ₂	268–305	12–330	72	1.9	<i>n.a.</i>	5.5	<i>n.a.</i>
H ₂ S	250–303	0.03–2.3	29	2.6	2.6 (2.6)	3.2	3.2 (3.2)
<i>i</i> -C ₄ H ₁₀	240–275	0.017–0.17	53	<i>n.a.</i>	<i>n.a.</i>	2.1	<i>n.a.</i>
<i>c</i> -C ₃ H ₆	237–290	0.008–0.57	35	<i>n.a.</i>	<i>n.a.</i>	1.1	<i>n.a.</i>

[†] Calculated using Klauda and Sandler correlation. [‡] Not available.

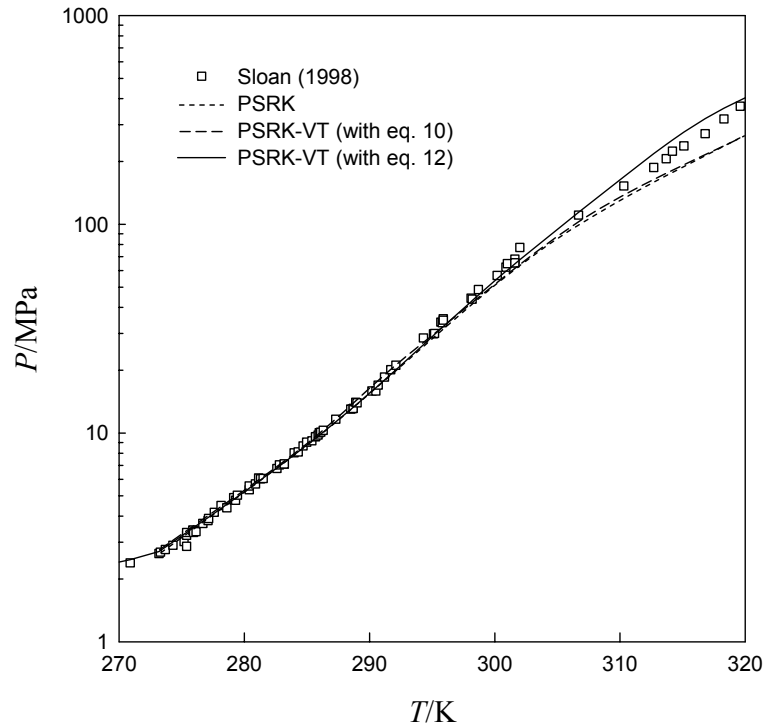


Figure 1. Comparison of experimental data with predicted results for methane hydrate in high pressure H–L_w–V region.

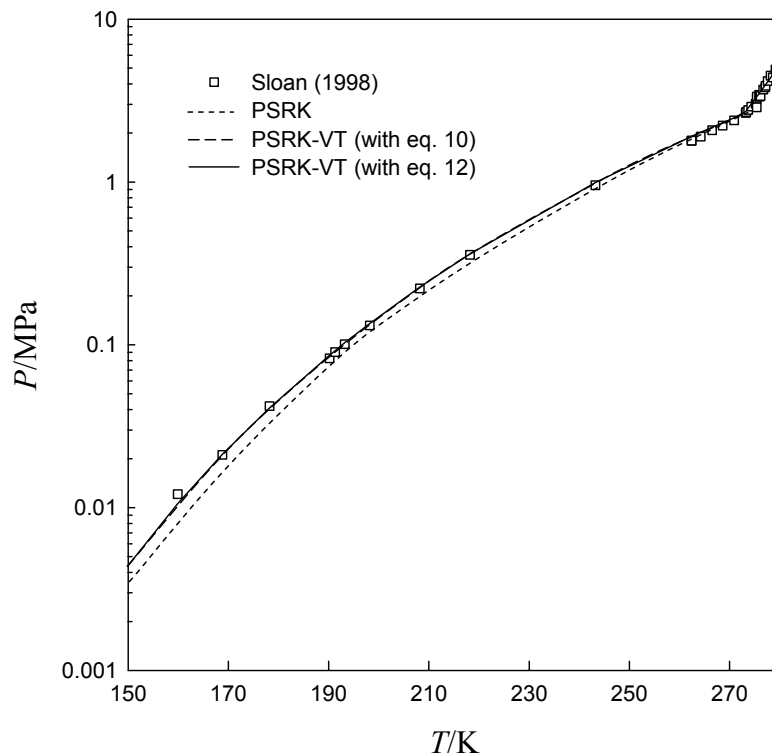


Figure 2. Comparison of experimental data with predicted results for methane hydrate in low pressure H–I–V region.

The % AADs between the measured and calculated dissociation pressures for simple hydrate-formers are presented in Table 2. Also listed in the table are the prediction results using four different models of MHV2, MHV2-VT, PSRK, and PSRK-VT. As mentioned previously, the MHV2 model considers gas components such as ethane and propane as new group components even though they can be treated without introducing new model parameters in the original UNIFAC frame. Therefore, we cannot calculate the phase equilibria of cyclopropane and isobutane hydrates because the interaction parameters between them and water have not yet been available. When using the PSRK model, it is possible to predict the hydrate dissociation pressures of all simple hydrate-formers including cyclopropane and isobutane. Since no actual experimental data of X-ray diffraction for sII hydrate depending on pressure have been reported, we investigate the effect of variable volume parameters on dissociation prediction only for sI hydrate. As can be seen in Table 2, it seems that the PSRK-VT and MHV2-VT models using the correlation suggested by Klauda and Sandler (2000) exhibit better correlation with experimental dissociation pressures than the PSRK and MHV2 models, especially for high pressure hydrate-formers such as methane and ethylene hydrates. However, the Klauda and Sandler correlation has still a large inaccuracy in dissociation prediction of methane hydrate at high pressure conditions, even though it is very effective for predicting the dissociation pressures at low pressure conditions as shown in Figures 1 and 2. In contrast, our correlation perfectly reproduces the dissociation behavior of methane hydrate at both high and low pressure conditions. This result implies that an

accurate description of hydrate molar volume depending on pressure as well as temperature must be considered to resolve inaccuracies in dissociation predictions at high pressure conditions. At extremely high pressures, noticeable errors may be caused by a very small change of hydrate molar volume because the effect of the Poynting correction would be of significance. We note that Klauda and Sandler (2000) have provided their correlation for hydrate molar volume by fitting the dissociation data for methane hydrate at high pressures, whereas our correlation is presented by fitting the experimental values from X-ray diffraction data for methane hydrate at high pressures.

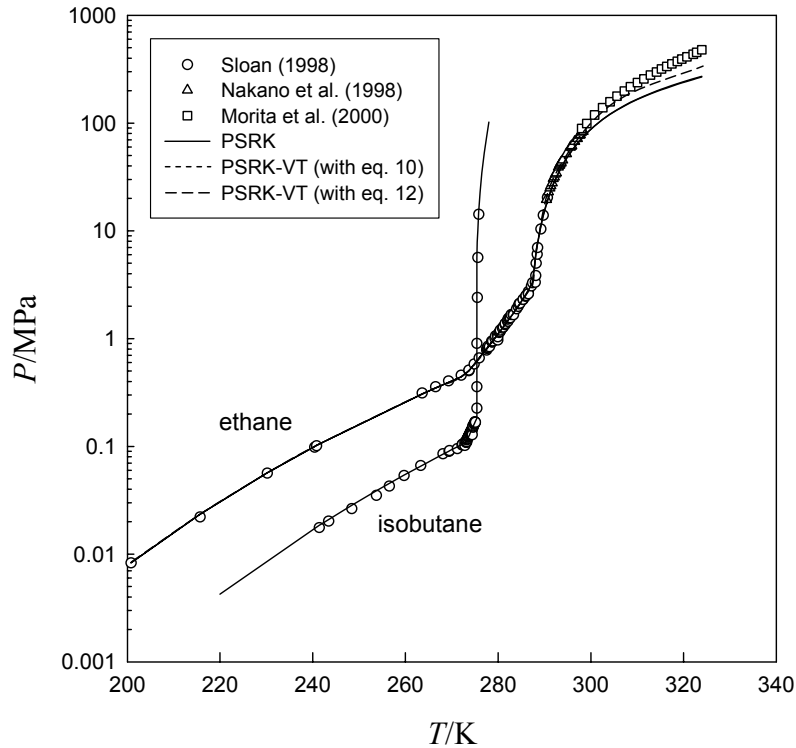


Figure 3. Comparison of experimental data with predicted results for ethane and isobutane.

Figure 3 shows the phase diagram for simple ethane and isobutane hydrates over a wide range of temperature and pressure. For isobutane hydrate, only the PSRK model is used to predict the dissociation behavior because the correlation for molar volume of sII hydrate is not available. As shown in Figure 3, all calculated results show an excellent agreement with the experimental data for both hydrate systems except high pressure region over 100 MPa for ethane hydrate. At higher pressures than 100 MPa, the predicted results of the PSRK-VT model with Eq. 12 are better than those of the PSRK and PSRK-VT models with Eq. 10 as easily expected. The erroneous prediction of the high pressure behavior of gas hydrate seems to be unavoidable for both PSRK and PSRK-VT models without an accurate representation of hydrate molar volume. Complete pressure-temperature behavior of cyclopropane hydrate is shown in Figure 4. The cyclopropane hydrate may be taken as a typical example for testing thermodynamic model, because it forms both sI and sII hydrates, depending on the formation condition. The PSRK model can predict accurately the entire phase behavior including the

structural transition as shown in Figure 4. One of the most surprising results is that a new quadruple point, thermodynamically unique and invariant condition, is carefully predicted to be 272.6 K and 7.55 MPa. At this quadruple point, four individual phases of sI hydrate (H_I), sII hydrate (H_{II}), liquid water (L_w), and ice (I) can coexist in equilibrium. Accordingly, four different three-phase boundaries of the H_I - H_{II} - L_w , H_I - H_{II} -I, H_I - L_w -I, and H_{II} - L_w -I curves can be successfully reproduced by the PSRK model as shown in Figure 4. Unfortunately the experimental evidence of phase behavior around the quadruple point has not yet been reported in the literature.

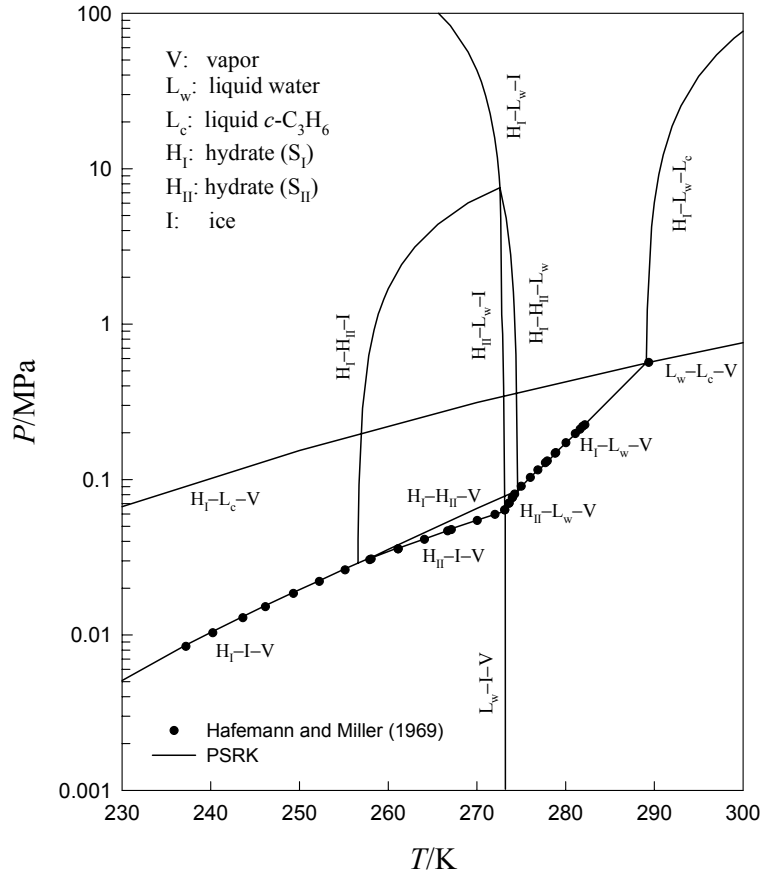


Figure 4. Complete p - T diagram of cyclopropane hydrate.

The % AADs of hydrate dissociation pressures predicted by both the PSRK and MHV2 models for the mixed guest systems are presented in Table 3. It can be easily seen that the % AADs of the hydrate systems in which the structural transition occurs are greater than those forming only one hydrate structure. For all mixed hydrate systems considered in this work, the prediction results of the PSRK model are more accurate than those of the MHV2 model. Particularly, for the ternary guest systems such as methane-propane-hydrogen sulfide and methane-carbon dioxide-hydrogen sulfide hydrates, the difference in deviation values between the PSRK and MHV2 models becomes larger. As stated early, this may be due to the inherent limitation of the MHV2 model that the guest-guest interaction is not taken into account. Thus, we can conclude that the interaction between guest molecules should be considered for accurately

predicting the dissociation behavior of mixed gas hydrates. Large deviations in the MHV2 model predictions may come from inappropriate assumption that all gas-gas interaction parameters are zero. In Table 4, we summarize the Kihara potential parameters for four different models considered in this study.

Table 3. Average Absolute Deviations of Predicted Phase Equilibria of Mixed Gas Hydrates

System	T , K	P , MPa	N_p	% AAD	
				MHV2	PSRK
CH ₄ -C ₂ H ₆	274–304	0.94–69	54	9.0	8.8
CH ₄ -C ₃ H ₈	270–305	0.15–69	78	4.7	3.4
CH ₄ -N ₂	273–296	3.6–36	63	12.5	12.3
CH ₄ -CO ₂	273–288	1.4–11	59	3.2	2.4
C ₂ H ₆ -C ₃ H ₈	273–284	0.44–2.1	60	10.6	10.2
C ₂ H ₆ -CO ₂	273–288	0.56–4.1	40	7.0	5.6
C ₃ H ₈ -N ₂	274–290	0.25–18	29	6.5	5.4
C ₃ H ₈ -CO ₂	273–287	0.30–4.3	37	6.5	6.2
CH ₄ -C ₃ H ₈ -H ₂ S	275–301	0.33–4.3	13	14.7	8.1
CH ₄ -CO ₂ -H ₂ S	279–298	1.4–16	37	41.4	14.5

Table 4. Fitted Kihara Potential Parameters for Gas-Water Interaction

Guest	a , * Å	MHV2		MHV2-VT		PSRK		PSRK-VT	
		σ , Å	ϵ/k , K	σ , Å	ϵ/k , K	σ , Å	ϵ/k , K	σ , Å	ϵ/k , K
CH ₄	0.30	3.2408	153.2	3.1872	155.6	3.2402	153.1	3.1718	157.0
C ₂ H ₆	0.40	3.4383	175.0	3.4333	174.9	3.4146	174.5	3.4149	174.5
C ₂ H ₄	0.47	3.3228	173.1	3.3114	173.1	3.2842	173.3	3.2827	173.3
C ₃ H ₈	0.68	3.4435	187.4	<i>n.a.</i>	<i>n.a.</i>	3.3445	196.5	<i>n.a.</i>	<i>n.a.</i>
C ₃ H ₆	0.65	3.4419	177.8	<i>n.a.</i>	<i>n.a.</i>	3.5446	173.9	<i>n.a.</i>	<i>n.a.</i>
CO ₂	0.72	2.9327	169.5	2.9318	169.5	2.9317	169.9	2.9305	169.9
O ₂	0.36	2.9580	133.2	<i>n.a.</i>	<i>n.a.</i>	2.9544	133.5	<i>n.a.</i>	<i>n.a.</i>
N ₂	0.35	3.1308	123.8	<i>n.a.</i>	<i>n.a.</i>	3.0958	123.5	<i>n.a.</i>	<i>n.a.</i>
H ₂ S	0.36	3.2000	201.7	3.2000	201.7	3.2000	201.6	3.2000	201.6
<i>i</i> -C ₄ H ₁₀	0.80	<i>n.a.</i>	<i>n.a.</i>	<i>n.a.</i>	<i>n.a.</i>	3.3872	190.6	<i>n.a.</i>	<i>n.a.</i>
<i>c</i> -C ₃ H ₆	0.50	<i>n.a.</i>	<i>n.a.</i>	<i>n.a.</i>	<i>n.a.</i>	3.4560	210.8	<i>n.a.</i>	<i>n.a.</i>

* Parrish and Prausnitz (1972)

Conclusion

In this article, we provide a new method for predicting the phase equilibria of gas hydrates using the PSRK group contribution model. The fugacity of all components in vapor and liquid phases coexisting hydrates is calculated by the PSRK group contribution method incorporated with the UNIFAC model. Based on the van der Waals–Platteeuw theory with the Kihara potential function, the fugacity equation of water in the hydrate phase, which is coupled with the PSRK model, can be used to accurately predict the dissociation behavior of simple hydrates. Since this approach takes into account the interaction between gas molecules with a help of the PSRK and UNIFAC model, it greatly improves upon the accuracy of the MHV2 model for mixed gas hydrates. In particular, for three-guest hydrate systems such as methane–propane–hydrogen sulfide and methane–carbon dioxide–hydrogen sulfide, the PSRK model resolves noticeable errors of the MHV2 model. This implies that the interaction between guest molecules should be considered for accurately predicting the

dissociation behavior of mixed gas hydrates. Dissociation prediction for the cyclopropane and isobutane hydrates is carried out using the PSRK model with the interaction parameter between them and water in the original UNIFAC frame. It is interesting to note that a new quadruple point for cyclopropane hydrate, which has not yet been reported, is predicted by the proposed model. An accurate representation for hydrate molar volume depending on temperature and pressure is provided. Using this equation, the error between experimental and calculated dissociation pressures for methane hydrate at high pressure conditions is reduced.

Acknowledgments

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